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(Contribution from the Chemistry Department of Florida State
University)

Preferential Solvation in Mixed Solvents. I. Activity and

Hydration of Sodium Chloride in 50% Dioxane-Water[1]

by A. L. Bacarella, Arthur Finch and Ernest Grunwald

ABSTRACT

We have measured orthobaric vapor pressures and vapor densities
for the system dioxane-water and have derived the equation of state
of the vapors. We have measured activities in the system NaCl-
50 wt % dioxane-water at 25.0°. The activity data indicate strong
preferential hydration of sodium chloride. The solvation theory of
Bjerrum[2] and Stokes and Robinson[3] has been extended to mixed
solvents and has resulted in a quantitative measure of relative
solvation by the solvent components. The hydration number of
sodium chloride at infinite dilution in 50 wt. % dioxane has been
found to be 40. The significance of this value is discussed in
relation to other values. The concentration dependence of the
activity coefficient of sodium chloride in 50 wt. % dioxane is
found to resemble that of sodium chloride in water at concentrations
greater than 0.1 m.

Introduction.- It has long been recognized that solvation has an important effect on the activity of solutes[2]. For aqueous

(2) See, for example: N. Bjerrum, Medd. K. Vetinskapsakad. Nobelinstitut, 5, #16, (1919).

solutions of electrolytes, the theory of Stokes and Robinson[3],

(3) R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc., 70, 1871 (1948)

which allows for the hydration of the ions, has achieved marked success in predicting activity coefficients over wide ranges of concentration. However, the solvation numbers derived from this theory are not in good agreement with solvation numbers deduced from other evidence[4,5]. The discrepancy is significant, and to

(4) J. O'M. Bockris, Quarterly Reviews, 3, 173 (1949).
(5) A. Eucken, Z. Elektrochem., 57, 6 (1948).

resolve it one should measure activity coefficients in systems in which more direct evaluation of solvation numbers is possible.

An ideal system for this purpose is one involving a two-component solvent, one component of which is non-solvating. The activity of a third (solute) component may be deduced from solvent vapor pressure data, and the solvent activity a_{12} is given[6] by

(6) J. N. Bronsted, "Physical Chemistry", Wm. Heinemann Ltd., London, 1937, p. 158.

$$a_{12} = \left(\frac{f_1}{f_1^o} \right)^{Z_1} \left(\frac{f_2}{f_2^o} \right)^{Z_2} \qquad (1)$$

where (f_1, f_1^o) and (f_2, f_2^o) are the fugacities of the two solvent

components in the presence and absence, respectively, of the solute.

Z_1 and Z_2 are the mole-fractions of the solvent components in the

absence of solute. Equation 1 assumes that Z_1/Z_2 remains constant

as solute is added[6]. If the solute is solvated by component 1

only, this will be indicated by an abnormally low value of f_1/f_1^o,

compensated by a corresponding increase in the value of f_2/f_2^o.

Thus the relative solvation of different solutes may be determined

from the departure of their respective fugacity ratios from equality.

Previous work in the system dioxane-water suggests that this

system approximates to the ideal situation. Mogling has found that

the addition of sodium chloride to aqueous dioxane results in an

increase of the vapor pressure of the dioxane[7]. Lucas & Hammett[8]

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(7) D. Mogling, quoted by M. Kortum-Seiler and G. Kortum,
    Z. Elektrochem., 54, 70 (1950).
(8) G. R. Lucas and L. P. Hammett, J. Am. Chem. Soc., 64,
    1928 (1942).

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have reported that the melting-point of dioxane in equilibrium

with 60 wt. % dioxane-water is raised by addition of certain elec-

trolytes. The work of Harned and co-workers has shown, however,

that in the higher concentration range the activity coefficient

curves for hydrochloric acid in aqueous dioxane resemble those

obtained in water.[9] This evidence suggests that the system dioxane-

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(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of
    Electrolytic Solutions", Reinhold Publishing Corp., New York,
    1943, chapter 11.

water is suitable for the simultaneous measurement of relative

solvation numbers and activity coefficients, and also that these

results might apply to electrolytes in pure water. In this paper,

the first of a series dealing with the problem, we present thermo-

dynamic data for the system NaCl-50 wt.% dioxane-water.

EXPERIMENTAL PART

We have derived values of a_{12} from measurements of the vapor

composition and vapor density. The equation of state of the vapors,

required for this purpose was obtained _via_ vapor pressure measurements.

Measurement of Vapor Pressure.- Since the data obtained differ

significantly from those recorded elsewhere[10], all relevant

(10) F. Hovorka, R. A. Schaefer, and D. Dreisbach, J. Am. Chem. Soc.,
    58, 2264 (1936).

experimental details are included. The static method was employed,

the pressure being measured on a differential mercury manometer of

internal diameter _ca._ 1 cm. Pressure differences were read using a

Gaertner cathetometer graduated to 0.05 mm., although in practice

it was found possible to extend the precision to $\mp$ 0.03 mm. The

sample of liquid was contained in a 10-ml. bulb attached to the main

apparatus _via_ a 14/36 ground joint. During a run the sample was

surrounded by a 3-liter Dewar containing water, the temperature of

which was maintained constant to within $\mp$ .005°C by a toluene regu-

lator of convential design. The high-vacuum side of the mercury

manometer was connected to a single-stage mercury diffusion pump,

backed by a Cenco-Hyvac pump. The pressure, measured by a McLeod

gauge, was ca. 10^{-5} mm. The three main sources of error inherent in static vapor pressure measurements—premature condensation of vapor (1), gas dissolved in sample (2), and contamination by grease from stop-cocks, etc. (3), were treated as follows.

(1) The connecting tube from the sample in the thermostat to the manometer was lagged with asbestos and wound with nichrome wire; by passing a suitable current a temperature of ca. 40°C was maintained. The manometer itself was surrounded by a Pyrex tube in which ether was refluxed. The temperature was measured by a thermometer placed in the vapor bath, and varied between 35.5 and 37°C. Since the highest temperature studied was 35°, these precautions are believed to be entirely satisfactory.

(2) Before introduction to the vapor pressure apparatus the sample was out-gassed in an auxiliary apparatus by repeated melting and freezing, followed by pumping. The sample was then transferred to the main apparatus, and a series of runs, each at varying temperatures, made. Between runs the vapor was condensed back into the sample bulb and pumped overnight at dry-ice temperatures with the high-vacuum system. It was found that in any series of runs on one sample the first two runs yielded values slightly higher than the (reproducible) values obtained with the succeeding runs. This was attributed to the completion of the out-gassing process, and consequently only the later runs were accepted. Finally, to ensure that no contamination resulted from small quantities of liquid trapped between the mercury in the walls of the manometer, the mercury was removed, cleaned, and dried at 60°C under vacuum between each series of runs.

(3) After preliminary experiments, Dow silicone grease was used in minimum quantities as lubricant for the stopcock and ground joint in the vapor system. As far as could be judged, no contamination resulted.

The composition of the sample was checked before and after each series of runs by refractometric analysis. The pressure readings were corrected to standard gravity, and the temperatures were measured on a thermometer recently calibrated by the National Bureau of Standards. As a final check of the apparatus, the vapor pressure of doubly-distilled, carbon-dioxide-free water was measured in the range 25-35°C. The average deviation of fifteen experimental values from accepted values[11] was -0.015 ± .032 mm.

(11) F. G. Keyes, J. Chem. Phys., 15, 611 (1947).

Measurement of Vapor Density.- The dynamic method of Washburn and Heuse was employed,[12] the apparatus being modified for use with

(12) E. W. Washburn and E. O. Heuse, J. Am. Chem. Soc., 37, 309 (1915).

two-component vapor systems. A slow (ca. 2000 ml. per hour) stream of dry nitrogen was passed, first through a series of saturators containing the test solution, and then through saturators containing the reference liquid, 50 wt.% water-dioxane. The vapor density of the reference liquid was determined separately by experiments using water, dioxane, and benzene as standards. The saturators consisted of

50-ml., 14-mm. internal diameter Pyrex tubes connected in pairs by
terminal U-tubes. Central 18/6 ground-glass ball joints enabled
sections of several pairs of saturators to be connected in series by
U-tubes bearing 18/6 socket joints. It was found that a volume of
20 ml. of liquid in each saturator was satisfactory; larger volumes
resulted in mechanical spray of liquid by the nitrogen. To reduce
further the danger of spray to negligible dimensions, the last two
saturators in any train were kept dry, and were connected to the
previous saturator via a spiral spray trap. The spray trap consisted
of a U connecting tube with 3 or 4 helical turns packed with pyrex
helices. Preliminary experiments determined the number of saturators
necessary to ensure complete saturation of the nitrogen. For example,
4 saturators were required to ensure water—water-vapor equilibrium;
an additional pair were added as guarantee. The saturated nitrogen
then passed through a pyrex cold trap of conventional design
immersed in a Dewar containing dry ice-acetone, and through a
Nesbitt absorber containing magnesium perchlorate. It then con-
tinued through a second series of saturators, cold trap, and Nesbitt
absorber before exit to air. Preliminary absorption experiments
showed (a) the cold trap gave quantitative pick-up of water and
dioxane and (b) the magnesium perchlorate absorber gave quantitative
pick-up of water and better than 98% pick-up of dioxane. Conse-
quently the Nesbitt absorber served both as a check for the cold trap
and as a safeguard against back-diffusion of vapor into the trap.
The entire apparatus was mounted on an angle-brass welded frame; a
longitudinal slot filed into the base of the frame fitted on to a

brass knife-edge. A driving motor and eccentric rocked the frame

about 10° from the vertical at 20 cycles per minute[13]. As the frame

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(13) A dynamic vapor pressure apparatus similar to the one described was first used by E. Grunwald while he was a summer visitor at the Brookhaven National Laboratory in 1950. We are indebted to R. W. White of the Brookhaven National Laboratory, Upton, N. Y., for the design of the rocking apparatus.

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rocked, alternately one end and then the other of the saturators

became blocked with liquid, forcing the nitrogen to flow into the

opposite direction. The assembled apparatus and frame was immersed

in a large water bath, the temperature of which was controlled to

within $\pm$ 0.002°C. A powerful 1/8 H.P. stirrer ensured that the

temperature uniformity of the bath was maintained to within the

limits detectable on a Beckmann thermometer. All connecting tubes

from the bath to the traps were wound with nichrome wire, through

which a suitable current was passed. This obviated any premature

condensation. When a suitable amount of vapor had been condensed the

flow of nitrogen was stopped, and the cold traps removed. After

equilibration to atmospheric temperature and pressure, the traps were

weighed to 1/10 mg. on an analytical balance. A standard technique

was developed for the weighing, and preliminary experiments showed

that the accuracy was within 1 mg.

Analysis of Water-Dioxane Mixtures.- The composition of water-

dioxane mixtures was determined optically, using a Bausch and Lomb

dipping refractometer, modified for use with small (ca. 6-ml)

samples. The samples were placed in a 10 ml. weighing bottle which

fitted into the metal beaker and over the refractometer prism.

When the metal beaker was placed in position, the samples were completely air- and water-tight. Readings were taken at 25.00 $\pm$ 0.005°C. The instrument was calibrated with 13 standard samples ranging from 80 - 90% dioxane. In this range, the curve of wt. % dioxane vs. refractive index was accurately linear; the mean deviation of the experimental points from the least-squares line corresponded to $\pm$ 0.016%. Portions of the standard samples were stored in evacuated ampoules for later use in comparison with the unknown samples. The reproducibility of the vapor compositions was well within the accuracy of the refractometric method. For example, the composition of the vapor condensate from 50% dioxane, taken over four determinations, was 83.459 $\pm$ 0.005%.

Materials.- Distilled water was redistilled from alkaline potassium permanganate solution and was protected from the atmosphere by a soda-lime tube.

Dioxane was purified by the method of Marshall and Grunwald[14].

(14) H. P. Marshall and E. Grunwald, J.Am. Chem. Soc., 76 (April, 1954).

Each batch was titrated for water ($\lesssim$ .02%) by the Karl Fischer method before preparation of the mixed solvents. Freezing-curve analysis showed that the mole fraction of total impurity was equal to the Karl Fischer titre for water. Refractive index:
$n_D^{25.00}$ = 1.42006; $n_D^{29.50}$ = 1.41796; m. p. 11.78°.

Benzene was purified by repeated crystallization and

distillation as suggested by Daniels, Matthews and Williams[15].

(15) F. Daniels, J. H. Matthews, and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941, p. 445.

A freezing point curve showed less than 0.02% impurity.

Sodium chloride was purified by the method of Kolthoff and Sandell[16]. Equivalent weight, using the Volhard method:

(16) I. M. Kolthoff and G. B. Sandell, "Textbook of Quantitative Inorganic Chemistry," The Macmillan Co., New York, 1948, p. 568.

$58.51 \pm .05$. (Calc. 58.45).

RESULTS

Vapor Pressure.- Vapor pressures were measured in the temperature range 25 to 35°C and are accurately represented by equations of the form

$$\log p = a - b/T \qquad (2)$$

Values of the constants a and b for pure dioxane, 50.00 weight % dioxane, and 70.50 wt. % dioxane are summarized in Table II. In order to confirm the accuracy of these measurements, the values of b were checked by comparison with values derived from partial molal heats of vaporization at 40° (Table I) calculated by us from the data of Amis & Stallard[17]. As shown in Table II, the agreement

(17) R. D. Stallard and E. S. Amis, J. Am. Chem. Soc., 74, 1781 (1952).

is satisfactory. The standard error of estimate of p from

equation 2 in the range 25 to 35° is calculated[18] to be about 0.1%.

(18) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, 1943, pp. 461, 502.

Equation of State.- Two problems arise in this connection:
(i) The determination of the virial coefficient for the dioxane-water interaction in the gas phase; and (ii) whether the vapor densities obtained in the dynamic apparatus are better described by the Dalton or the ideal-solution law[19].

(19) M. A. Päul, "Principles of Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1951, pp. 309-317.

In order to determine which law best describes our gaseous solutions containing vapor and nitrogen at a total pressure of 1 atm, we have measured the ratio, d/d_w, of the vapor density of pure benzene or dioxane to that of water at 25.00°. These results are summarized in Table III, together with the second virial coefficients, B, the orthobaric vapor pressures, p^o, the vapor pressures corrected to 1 atm, $p^o_{1\,atm}$, and values of d/d_w calculated from these data using Dalton's law and the ideal solution law. As is apparent from the Table, the experimental values for dioxane are represented satisfactorily on either basis, but the values for benzene are not adequately represented by the ideal-solution law, yet agree well with Dalton's law. The discrepancies from Dalton's law are of the order of 0.2% and may be ascribed to experimental error in the vapor pressure measurements. We have therefore used Dalton's law in all further calculations.

Table I

Partial Molal Heats of Vaporization[a] in the System Dioxane-Water, 40.0°

Mole % Dioxane in		$\bar{L}$ (int. joules/mole) for	
Liquid	Vapor	Dioxane	Water
0.00	0.00	42.00	43.34
1.58	12.46	41.98	43.34
4.19	23.70	40.64	43.38
7.12	33.27	40.24	43.40
11.52	41.22	38.48	43.58
16.67	47.33	36.71	43.87
40.64	55.72	36.74	43.86
100.00	100.00	38.59	-

a) Calculated from data of ref. 17.

Table II

Constants in the Vapor Pressure Equation 2

Dioxane, weight %	a (obs)	10^{-3}b (obs)	10^{-3}b(calc)[a]
100.00	8.3159	2.0148	2.016
70.50	8.8032	2.1285	2.141
50.00	8.9123	2.1734	2.105

a) Calculated from heats of vaporization (Table I).

Table III

Test of Dalton's Law and Ideal-Solution Law for Gaseous Solutions,

25.00°.

Liquid	B (ml/mole)	p° (mm)	$p^{\circ}_{1\ atm}$
Water[a]	-1163	23.752	23.769
Benzene[b]	-1415	95.25	95.55
1,4-Dioxane	-1690[c]	36.18[d]	36.30

Liquid	d/d_w (obs)	Dalton's Law	Ideal Solution
Benzene	17.57	17.53	17.27
1,4-Dioxane	7.47	7.48	7.48

a) Higher virial coeffs.: $C = -894$ ml atm^{-1}; $D = -40.1$ ml atm^{-2}; ref. 11.
b) Ref. 20, 21.
c) B was estimated as -1680 ml from critical constants[22] and the Berthelot equation, and as -1694 ml by equation 2 of Scott et al[23]. An average value is listed.
d) From data in Table II.

(20) P. G. Francis, M. L. McGlashan, S. D. Hamann and W. J.McManamey, J. Chem. Phys., 20, 1341 (1952).
(21) a. E. R. Smith, J. Research Nat. Bur. Standards, 26, 129 (1941)
    b. C. B. Willingham, W. J. Taylor, J. M. Pignoco, and F. D. Rossini, ibid., 35, 219 (1945).
    c. J. H. Baxendale, B. W. Enustun and J. Stern, Trans. Roy. Soc. (London), A248, 169 (1950).
    d. P. W. Allen, D. H. Everett and M. F. Penney, Proc. Roy. Soc. (London), A212, 149 (1952).
(22) W. Herz and S. Lorentz, Z. physik. Chem., A140, 406 (1929).
(23) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie, and H. M. Huffman, J. Am. Chem. Soc., 72, 2424 (1950).

By analogy with the behavior of other gaseous hydroxylic substances[24], hydrogen-bonding of water to dioxane is expected, and

(24) C. B. Kretschmer and R. Wiebe, J. Am. Chem. Soc., 76, (1954).

the association constant may be large enough to be significant. This constant was therefore determined from vapor-density and vapor-pressure measurements of aqueous dioxane. The density of 50.00 wt.% dioxane, determined by comparison with pure benzene, dioxane and water was 0.1224, 0.1228 and 0.1226$_5$ g/l, respectively. The discrepancy between these figures is probably due to uncertainties in the vapor pressures of these liquids. An average value, 0.12260, was used in Table IV and in further calculations.

Table IV

Equilibrium Constant for Dioxane-Water Association, 25°

Wt.% Dioxane --		$p^o_{1\ atm}$	d	$10^4 K^b$	$p^o_{1\ atm}$
Liquid	Vapor	(mm Hg)^a	(g/l)	(mm Hg)$^{-1}$	(calc)^{b,c}
50.00	83.459	42.04$_6$	0.12260	9.4	42.072
70.50	87.365	46.27$_5$	0.14861	8.1	46.241

a) Computed from data in Table II and partial molal volumes in ref. 10.
b) Computed using Dalton's law and virial coefficients in Table III.
c) $K = 8.8 \times 10^{-4}$.

The relevant data are summarized in Table IV. The data indicate that the vapors are associated to the extent of about 2% in these systems, the value of K being $(8.8 \pm 0.7) \times 10^{-4}$. Equations 3 and 4 were used in these calculations.

$$p^o_{1 \text{ atm}} = p_1 + p_2 + K \, p_1 p_2 \qquad (3)$$

$$d_1 = d \, w_1 = (1 + K \, p_2) \, \frac{M_1 \, p_1}{RT + B \, p_1 + \ldots}$$

$$d_2 = d \, w_2 = (1 + K \, p_1) \, \frac{M_2 \, p_2}{RT + B \, p_2} \qquad (4)$$

In equations 3, 4, and all subsequent equations, the subscripts 1 and 2 refer to water dioxane, respectively, and w is the weight fraction of the component in the vapor. The last column of Table IV lists values of $p^o_{1 \text{ atm}}$, calculated from the average value, $K = 8.8 \times 10^{-4}$. The close agreement between these and the experimental values of $p^o_{1 \text{ atm}}$ confirms the adequacy of equations 3 and 4 in describing the vapor pressure—vapor density relationships.

K is of a reasonable magnitude. The association constants of other hydroxylic vapors, ROH, as estimated from virial coefficients[11,24] according to Woolley[25], range from 0.63×10^{-4} for R $=$ H to

(25) H. W. Woolley, J. Chem. Phys., **21**, 236 (1953).

1.83×10^{-4} for R $= \underline{i} - C_3H_7$. The somewhat greater dioxane—water constant is consistent with the better donor—acceptor properties and statistical factors of these molecules.

Data for NaCl - 50 wt.% Dioxane.- The experimental vapor
compositions and weight ratios relative to 50 wt.% dioxane at 1 atm
are shown in Table V. To test the internal consistency of these
data, we have prepared large scale plots of these quantities vs.
molality. The points fall on smooth curves, the mean and maximum
deviations being 0.024% and 0.18% for the weight ratios, and 0.015%
and 0.05% for the vapor compositions. Values of a_1, a_2, and a_{12} were
calculated from these curves at rounded concentrations by a method
of successive approximations. Starting with the weight ratio and a
first approximation to the total vapor pressure, d was calculated
for the salt solution, using the data for 50 wt. % dioxane in
Table IV. The partial and total pressures were then calculated from
d via equations 3 and 4, and d recalculated using the new total
pressure. The process was continued until the required values
converged.

f_1 and f_2 were calculated from p_1 and p_2 using the virial
coefficients in Table III, and a_1 and a_2 from the ratios $f_1/f_1^{\,o}$,
and $f_2/f_2^{\,o}$. Finally a_{12} was calculated from equation 1. The molal
activity coefficient of NaCl, referred to 1.0 m   NaCl, were
obtained from the expression

$$\log y/y_{1m} = - \int_1 \frac{33.428}{2\,m}\ d \log a_{12} - \log m \qquad (5)$$

by numerical integration, using both Weddle's and Simpson's method[18].
The two procedures gave almost identical integrals, and an average
value was taken. The results are shown in Table VI.

Table V

Experimental Results at 25.00°

Dioxane Wt.%	NaCl m	Weight Ratio[a]	Vapor Compos. W_2
50.00[b]	0.0000	1.0000	0.83459
	.1263	1.0350	.84250
	.2544	1.0669	.84903
	.3946	1.0982	-
	.4120	1.1008	.85646
	.5650	1.1334	.86288
	.8345	1.1882	.87270
	1.0041	1.2224	.87840
	1.2076	1.2612	.88486
50.00[c]	.0218	1.0077	.83631
	.0228	-	.83653
	.0232	1.0072	.83674
	.0482	1.0146	.83847
	.1418	1.0385	-
	.1497	-	.84348
	.1509	1.0413	.84380
	.2570	1.0652	-
	.2570	1.0658	.84870
	.2741	1.0698	.85021
50.63	.0000	1.0102	.83658
50.63	.2456	1.0728	.85054
51.12	.0000	1.0154	.83782
60.31	.0000	1.1287	.85846
70.50	.0000	1.2193	.87365

a) Relative to 50.00 wt. % dioxane = 1.0000, and corrected to atmospheric pressure = 760.0 mm.
b) Series A
c) Series B

Table VI

Activity Data at 25.00°

Dioxane, Wt. %	NaCl, m	a_1	a_2	a_{12}	y/y_{1m}
50.00	.000	1.0000	1.0000	1.0000	-
	.025	.9948	1.0110	.9976	-
	.050	.9900	1.0196	.9950	2.2
	.080	.9870	1.0295	.9941	1.8
	.100	.9855	1.0357	.9938	1.6
	.150	.9816	1.0513	.9931	1.13
	.200	.9759	1.0663	.9907	1.08
	.300	.9633	1.0956	.9846	1.08
	.400	.9517	1.1239	.9790	1.067
	.500	.9410	1.1515	.9738	1.041
	.600	.9305	1.1780	.9685	1.022
	.800	.9099	1.2290	.9575	1.010
	.900	.9005	1.2545	.9526	.998
	1.000	.8900	1.2799	.9466	1.000
	1.2076	.8676	1.3305	.9330	1.033
50.63	.000	.9975	1.0123	-	-
51.12	.000	.9948	1.0189	-	-
60.31	.000	.9597	1.1572	-	-
70.50	.000	.9215	1.2693	-	-

Further data for the System Dioxane-Water.- In the interpretation of the results for the salt solutions it was desirable to know the rate of change of a_1 and a_2 with solvent composition. We have therefore studied a number of solvents in the composition range 50.00 to 70.50 wt. %. The results are included in Tables V and VI.

Error Analysis.- The average reproducibility of a single mass-ratio determination was found to be $\pm$ 0.03% over 8 duplicate experiments. The average reproducibility of vapor composition was similarly estimated to be $\pm$ 0.015%. From these figures the average reproducibility of a_{12} was calculated to be $\mp$ 0.07%, and the resultant error in y is given by

$$(\log_{10} y) = 5.1 \times 10^{-3}/m \qquad (6)$$

Equation 6 is in agreement with the well-known fact that solute activity coefficients derived from solvent activity data became increasingly inaccurate with decreasing concentration. This effect is illustrated for our data in figure 1, where the dotted lines represent the limits of error in the value of the logarithm of the activity.

In the present experiments the accuracy is limited by the accuracy of measurement of the vapor composition. Suitable refinements in instrumental technique, for example the use of an interferometer instead of a dipping refractometer, would therefore result in still greater precision. On the other hand, the weight ratios and changes in vapor composition are almost independent of the solvent composition over ranges far in excess of the

reproducibility of the 50 wt. % dioxane solvents. This effect is illustrated by data for 50.63% dioxane in Table V, and no significant loss of accuracy is therefore to be expected from this cause.

DISCUSSION

<u>The Relative Solvation Index</u>.- The results in Table VI strikingly illustrate the effects of preferential solvation. While a_{12} decreases in a "normal" manner upon addition of solute, a_1 decreases abnormally fast, and a_2 actually increases. To account for this behavior, we have developed a theory of solvation, modeled upon similar theories for aqueous solutions[2,3], which permits quantitative evaluation of the relative solvation by the two solvent components. The theory assumes that, in the absence of solvation, a_1, a_2 and a_{12} will all be equal. Due to solvation, the amount of solvent in a system consisting of m moles of solute and 1000 g of 50% dioxane is reduced to $1000 - (n_1 M_1 + n_2 M_2)m$, where n_1 and n_2 are the solvation numbers per mole of solute, and M_1 and M_2 are the molecular weights. The "true" molalities m_3 and m_w of solute and water are therefore

$$m_3 = m/(1 - \chi m), \tag{7}$$

$$m_w = (m_w^o - n_1 m)/(1 - \chi m), \tag{8}$$

where $\chi = (n_1 M_1 + n_2 M_2)/1000$. The activities a_1 and a_2 may be written as functions of m_3 and m_w. Thus, for a_1,

$$\frac{d \ln a_1}{dm} = \left(\frac{\partial \ln a_1}{\partial m_3}\right)_{m_w} \frac{d m_3}{d m} + \left(\frac{\partial \ln a_1}{\partial m_w}\right)_{m_3} \frac{d m_w}{d m}$$

By supposition, $\partial \ln a_1/\partial m_3 = \partial \ln a_{12}/\partial m_3$. Therefore from

equations 7, 8, 9, and the Gibbs-Duhem equation, we obtain for

<u>dilute</u> solutions

$$\frac{d \ln a_1}{d m} = - \frac{1000\,\nu}{M_{12}(1 - \times m)^2} \left[1 + m (1 - \times m) \frac{\partial \ln y_3}{\partial m} \right]$$

$$- \frac{\beta}{2(1 - \times m)^2} \frac{\partial \ln a_1}{\partial m_w} \tag{10}$$

In (10), ν is the number of ions per molecule of solute, M_{12} is

the molar weight of the solvent, and β is defined by

$$\beta = 2(n_1 - \times m_w^{\,o}) \tag{11}$$

$$\beta = n_1 - n_2 M_2/M_1 \quad \text{(for 50\% dioxane)} \tag{11a}$$

At infinite dilution $\partial \ln y_3/\partial m = 0$, and $\partial \ln a_1/\partial m_w$ is

readily accessible from activity data for the solvent system with-

out added solute. For sodium chloride in 50% dioxane, equation 10

then reduce to

$$-\left(\frac{d \ln a_1}{d m}\right)_{m=0} = 0.05982 + \frac{\beta}{2}\left(\frac{\partial \ln a_1}{\partial m_w}\right)_{m=0} \tag{12}$$

The equations involving a_2 are entirely analogous to 10 - 12,

with a_2 substituted for a_1. Thus there is a relationship between

the effect of added solute and of added water on the activity of

the solvent components. This relationship is extra-thermodynamic

and may be tested by comparing β from data for component 1 with

the independent value of β for component 2. The relevant data

for sodium chloride in 50% dioxane are gathered in Table VII. The

two values of β are in satisfactory agreement, considering the

uncertainty in the evaluation of the derivatives, thus supporting

the present solvation theory.

The physical significance of the coefficient β (defined by

equation 11a) is of especial interest. β is zero in the total

absence of solvation, or when $n_1 = n_2 M_2/M_1$. It is positive when

solvation by water outweighs that by dioxane, $(n_1 > n_2 M_2/M_1)$, and

negative in the opposite case. β is therefore a measure of the

relative solvating efficiency of the two solvent components, and

we have therefore called it the relative solvation index.

Measurements of β for other electrolytes are in progress.

Table VII

Calculation of Relative Solvation Index for Sodium

Chloride in 50.00 wt.% Dioxane

Solvent Component	$\left(\dfrac{\partial \ln a}{\partial m_W}\right)_{m \,=\, o}$	$\left(\dfrac{d \ln a}{d m}\right)_{m \,=\, o}$	β
Water	.0066	-.20$_4$	43
Dioxane	-.031	.49	36

The Solvation of Sodium Chloride.- Although β does not lead

to the absolute value of n_1, it defines a lower limit. Thus for

sodium chloride at infinite dilution in 50% dioxane, $n_1 \geqslant 40$.

This number is more reasonable than the value 3.5, obtained for

sodium chloride by Stokes and Robinson[3]. It seems logical to

identify n_1 with the number of electrically saturated water

molecules trapped in the immediate vicinity of the two ions[26,27].

(26) T. J. Webb, J. Am. Chem. Soc.; 48, 2589, (1926).
(27) P. Debye "Polar Molecules", Dover Publications, New York, 1945, chapter 6.

The volume of this region may be estimated from the dielectric constant of dilute salt solutions[27]. Recent measurements[28] give

(28) W. J. Dunning & W. J. Shutt, Trans. Faraday Soc., 34, 467 (1938).

the volume as 560 cu.A$^\circ$ per ion for potassium chloride in water, from which the hydration number is estimated to be ca. 35 for the two ions. Since the hydration number of sodium chloride should be somewhat greater, our figure, $n_1 \approx 40$, is reasonable. The dielectric constant data indicate a strong tendency for two or more ions to share the same solvation shell, even at fairly low concentrations[28]. One can therefore expect a progressive decrease in average solvation number with increasing concentration, and this effect may partially account for the low value obtained by Stokes and Robinson[3]. The effect is illustrated very clearly by density data for the system NaCl-supercritical steam[29]. The hydration

(29) C. S. Copeland, J. Silverman, and S. W. Benson, J. Chem. Phys., 21, 12 (1953).

number of sodium chloride at 396°C and 275 atm, estimated from partial molal volumes, decreases from 70 to 40 in the concentration range 1.0 to 6.74% NaCl.

<u>Activity Coefficients in Concentrated Salt Solutions</u>.- In
figure 2 we compare the variation of log y/y_{1m} with concentration
and solvent composition for sodium chloride and hydrochloric acid
in the system dioxane-water. The new data for sodium chloride
confirm the previous indication that the concentration dependence
of activity in concentrated solution is characteristic of the
electrolyte, but largely independent of the solvent composition.
The two curves for hydrochloric acid are closely parallel, and the
two curves for sodium chloride are nearly so. Each set of curves,
however, differs markedly from the other. This shows that at high
concentrations the activity coefficient is not primarily a function
of the dielectric constant of the medium, but depends largely on
factors, such as solvation, which are characteristic of the
electrolyte.
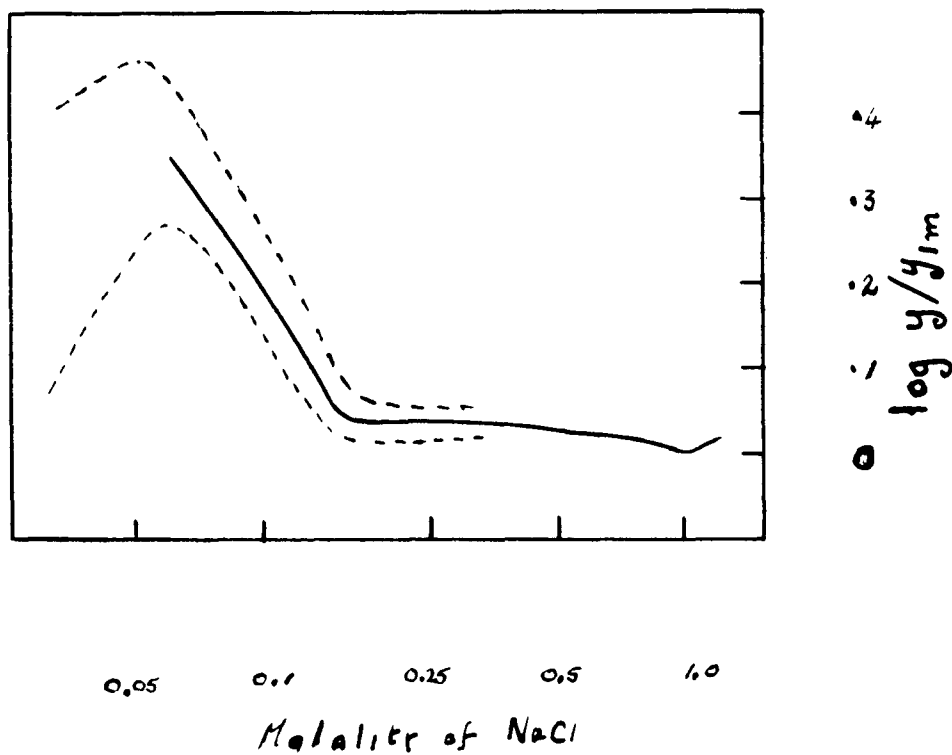
Tallahassee, Florida

FIGURE 1

$\log y/y_{1m}$

.4

.3

.2

.1

0

0.05   0.1   0.25   0.5   1.0

Molality of NaCl

Fig. 1.-Plot of log y/y_{1m} vs. m for sodium chloride in
50 wt. % dioxane at 25.00. The dotted lines show
the limits of error.

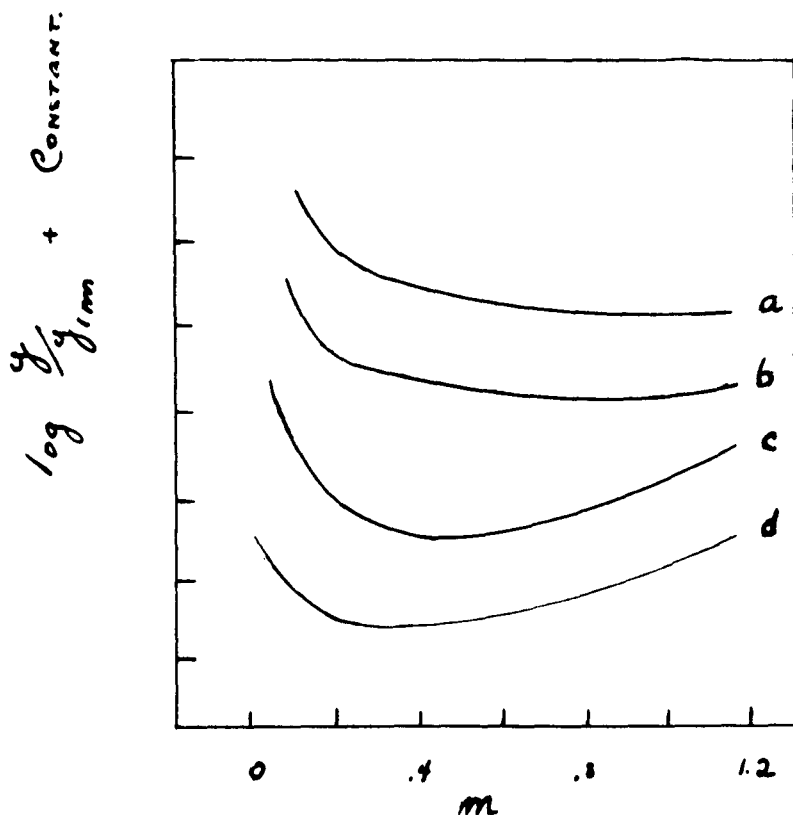Fig. 2.--Plot of log y +constant $\underline{vs}$.m, 25.0°. Curve (a) NaCl, water;
(b) NaCl, 50% dioxane; (c) HCl, 45% dioxane; (d) HCl, water.
Scale of the ordinate: 1 scale division = 0.05 unit.